1. Introduction

Pesticides are the chemicals used in agriculture, to protect the crops from the attack of pest, diseases and rodents. They are toxic and cause environmental contamination as well as generate public health problems. The analysis of pesticide residues in water is difficult since these compounds occur at very low concentration levels[1].Pesticides are worldwide used to prevent the croppers, forestry and horticulture from the damages of insects, diseases, fungi, and other pests to adjust the growth of the plants or to increase the yield of the croppers. However, it has to take into account that only a small part of the applied pesticides reaches its final destinations, the biological targets. Herbicides such as alachlor, atrazine,cyanazine and metalachor were the most prevalent. The residual pesticides are still toxicologically active and remain in the environment, hence must be destructed in the ecosystems to prevent accumulation or contamination, therefore pesticides are the essential parts of xenobiotic brought into the environment by human activities, further the most potential sources of risk can be found with the manufacturing plants, which may emit pesticides resulting in a large scale soil and ground water contamination [2].

Depending on the chemical compositions of pesticides, they exhibit different extents of toxicity to humans as well as animals. Some pesticides have been found to affect the nervous system on human beings and animals [3]. Pesticides enter into the environment either by direct or indirect application. The direct sources include runoff from agricultural fields, spray, drifts, rain water, sewage and effluents from industries, manufacturing pesticides or using them in their process.[4] Most pesticides are designed to harm or kill pests because some pests have similar systems to that of human beings and some pesticides can harm or kill humans.[5]. The wide range of pesticides or herbicides in use, makes research extremely

difficult for producing a single method for removal of herbicides or pesticides that applies universally. Several methods either independent or in conjunction have been used for the removal of these materials including chemical oxidation with ozone [6], photo degradation [7],combined ozone and UV irradiation [8],Fenton degradation[9],biological degradation[10],coagulation [11], and adsorption[12-14].Adsorption on activated carbon is the most widespread technology used to deal with purification of water contaminated by pesticides and other hazardous chemicals[14-17].However, due to high cost of activated carbon, its use in the field is sometimes restricted on economical considerations.

In the present study an industrially viable, cost effective, and ecofriendly adsorption technology using super paramagnetic nano particles of iron oxide loaded poly (styrene-co-acrylic). Hydrogel (super paramagnetic PSA Hydrogel) as adsorbent for the adsorption of pesticide from aqueous solution. Super paramagnetic iron oxide nano particles[mostly magnetite (Fe_3O_4) or maghemite (Fe_2O_3)] with tailored surface chemistry have been widely used experimentally for numerous applications. All application require that these nano particles should have high magnetization values and sizes smaller than 100nm with over all narrow particles have uniform physical and chemical properties. Because of large surface area to volume ratio, the magnetic nano particles tend absorb toxic pesticides.

Hydrogel

Hydrogels are water swollen hydrophilic polymer chains connected to each other via primary bonds (covalent) and secondary interactions (Vander Waal, electrostatic, hydrogen bonding etc).Amongst the polymers, Hyrdogel, known as 3-D cross linked polymer network attract special attentions, due to the lavish number of pesticide-binding functional groups in the network

such as SO_3, -OH, -COOH,-SH, NH_2, and the ability of tune the hydrophlicity and the porosity. The Hydrogel template can have additional characteristics such as biocompatibility, environmental sensitivity and ecofriendly and have applications as drug delivery material in cosmetics, tissue engineering and even separation of toxic species from water for purification purpose.

Nanoparticle of Iron oxide-

Magnetic (Fe_3O_4) nanoparticles have long been a subject of scientific and technological interest because of their unique magnetic and electric properties as well as numerous applications in the field of data storage, ferrofluids ,nano adsorbents, MRI, biomedicine, biosensor, bio-separation etc. Various methods have been developed during the past years to synthesize specific application based magnetic nanoparticles with desired size, acceptable size distribution and negligible particle aggregation. Recently, there has been a growing interest towards the use of magnetic nanoparticles for adsorptive removal of a variety of contaminants including pesticides and organic dyes from waste water owing to their several advantages over bulk magnetite particularly with respect to higher adsorption capacity and less time for adsorption equilibrium.

Iron oxide nanocrystals are of considerable interest in nanoscience and nanotechnology because of their nanoscale dimensions, nontoxic nature and superior magnetic properties.

Objectives-

The proposed synopsis includes the following objectives.

1. Synthesis of styrene based copolymer and insitu magnetization of co-polymer.

2. Synthesis and Characterization of crosslinked hydrogel by FTIR, TEM and SEM analysis.

3. Study of removal of pesticides such as Captan, Atrazine, Monocrotophas, DDT, Methyl parathion, Endosulphan, Dichlorvas, etc.

4. Study of dynamics of adsorption of pesticides onto hydrogel and to observe the influence of various experimental conditions on the adsorbed amount of pesticides.

5. Study of different factors like pH, time, temperature, concentration etc.

6. Study of adsorption by flow method (column).

A BRIEF REVIEW OF THE WORK ALREADY DONE IN THE FIELD:

Dikla Zadaka, Shlomo Nir etal in2008) studied atrazine removal from water by two polycations pre-adsorbed on montmorillonite. Batch experiments demonstrated that the most suitable composite poly (4-vinyle pyridine-co- styrene) montmorillonite (PVP-co-59%-mont) removed 90-99% of atrazine (0.5-28ppm) within 20-40 min at 0.367%w/w.Calculations employing Langmuir's equation could simulate and predict the kinetics and final extents of atrazine adsorption.

Hugues Humbert, Herve Gallard etal studied the removal of natural organic matter (NOM) and pesticides by the combination of anion exchange resins (styrene -co-acrylic acid) and powdered activated carbon (PAC).Experiments were conducted with high dissolved organic carbon (DOC) surface water (about 6.0mg DOC/L) spiked with both atrazine and isoproturon. Experiments conducted with high(200µg/L) and low (1µg/L) initial pesticide concentrations showed that simultaneous and successive combinations of anion exchange resine (AER) and PAC

significantly improve the removal of both pesticides compared with PAC treatment on row water.

Vinod K. Gupta, Imran Ali etal studied the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) and carbofuran from aqueous solution by using fertilizer industry waste and steel industry wastes as adsorbent in batch. Adsorption equilibrium kinetics, and thermodynamics were investigated as a function of initial pH, temperature, and pesticide concentrations. Equilibrium data fitted well to the Langmuir equilibrium model in the studied concentration range of 2,4-D and carbofuran at all the temperature studied.

Proposed Methodology

The methodology may be described as follows.

Materials

1. **Preparation of Nanoparticle of iron oxide:**

   A stock solution will be prepared by dissolving ferrous chloride and ferric chloride and the magnetic particles will be synthesized by adding ammonia solution with constant stirring. The magnetic particles so produced will be washed several times with double distilled water and stored.

2. **Preparation of Hydrogel:** Hydrogels are water swollen hydrophilic polymer chains connected to each other via primary bonds (covalent) and secondary interactions (Vander Waal, electrostatic, hydrogen bonding etc).styrene will be co-polymerised with acrylic acid and then this co-polymeric Hyrdogel will be washed with distilled water and cut into uniform size pieces. For in situ magnetization, these pieces were equilibrated in an

aqueous solution of ferrous chloride and ferric chloride for 24 hr. The magnetic hydrogel will be washed thoroughly with distilled water, dried and crushed into a fine powder.

3. Adsorbate:

Various pesticides solution such as Captan, Atrazine, DDT, Methyl parathion, Monocrtophas, and dichlorvas etc.

4. Batch Method of adsorbent:

The adsorption experiments will be conducted by shaking of adsorbate with a definite amount of hydrogel in aqueous medium. After equilibrium the residual amount of adsorbate in supernatant will be estimated spectrophotomatrically. The amount of adsorbed pesticides will be calculated by the following mass balance equation -

$$\text{Adsorbed amount (mg/g)} = \frac{(Ce - C_0) \times V}{m}$$

Where

C_0 = Concentration of pesticide (mg/ml)

C_e = equilibrium concentration of pesticide (mg/ml)

V = volume of adsorbate solution.

m = mass of the adsorbent.

Effects affecting adsorption

(1) **Effect of pH:-** The change in solution pH may also change properties of pesticide molecules. The surface functional groups of adsorbate make adsorption complicated by the charge characteristics of the adsorbent surface. The values of pH affect the surface properties of the sorbent.

(2) **Effect of adsorbent dose:-** Adsorbent dose is an important parameter because it determinations the capacity of an adsorbent for a given initial concentration of the adsorbate.

(3) **Effect of contact time:-** In order to study the effect of contact time on concentration of pesticides sorption, the experiments will be conducted for various time intervals at fixed concentration and fixed pH.

(4) **Effect of temperature: -** Temperature plays an important role on retention of pesticides by adsorbent. Effect of temperature on the removal of pesticides will be studied by conducting adsorption experiment at different temperatures in the range from 10 to 50^0 C.

(5) **Effect of initial concentration:-**The adsorbate and adsorbent interaction will be studied by performing the adsorption experiment with different concentration as on increasing the concentration of solute, greater number of pesticides arrives at interface and thus get adsorbed.

Modeling of adsorption isotherm- Sorption isotherm is a functional expression that correlates the amount of solute sorbed per unit amount of the sorbent and the concentration of sorbate in bulk solution at a given temperature under equilibrium condition. The sorption data will be subjected into different isotherm namely-

Langmuir isotherm

Freundlich isotherm

Adsorption kinetics- The kinetics of adsorption is important as it control the process efficiency. For evaluating the adsorption kinetics of pesticides, the following two models-

Pseudo-first-order Lagergren

Pseudo-second-order

Column studies: -

The experiment will be performed using a column, 10 cm in height and 1 cm in diameter. The column will be filled with hydrogel. The pesticides solution will be collected at different time intervals and the concentration of pesticides will be determined spectrophotomatrically.

Factor affecting adsorption

Effect of bed height: Accumulation of pesticides in the fixed bed column is largely dependent on the quantity of sorbent inside the column. it will be studied that bed capacity and exhaustion time increasing with increasing bed height, as more binding site are available for sorption, the increasing in adsorption with that in bed depth was due to the increase in adsorbent dose.

Effect of initial concentration: An increase of the initial pesticide concentration when experimental conditions are kept constant, significantly affected the breakthrough curve.

Effect of bed height-Accumulation of pesticides in the fixed bed column is largely dependent on the quantity of sorbent added in the column.

EXPECTED OUTCOME: The proposed work basically aims are-

(1) Indiscriminate use of pesticides in the modern agricultural practices leads to several environmental problems. One of such problems is the contamination of surface and ground water by pesticide. The contamination of surface water and ground water sources with various pesticides is posing a direct threat to human health. Adsorption is considered to be one of the important purification and separation process.

(2) To improve the removal efficiencies / Adsorption capacities of such prepared adsorbents after chemical modifications or appropriate treatment.

(3) Cost factor is also an important point that should be considered before selecting such developed adsorbent in water pollution control.

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Signature of the Supervisor

5.8.13

Dr.(Smt.) Alka Tiwari
Professor
Department of Chemistry
Govt. V. Y. T. P.G. Auto., College,
Durg(C.G.)

Dr. Alka Tiwari
Professor,Chemistry
Govt.V.Y.T.PG.Auto.College
DURG(C.G.)

Signature of the Candidate

5.8.13

Anita Bind

Forwarded

Chairman, DRC

GOVT. V. Y. T. P.G. AUTONOMOUS COLLEGE, DURG (C.G.)

2013

Principal
Govt. V.Y.T.P.G. Auto.College
Durg (C.G.)

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